

(12) International Patent Applications which are Public as
per the Contractual Agreement of the Patents Contract

(19) World (Global) Intellectual Proprietary Rights
Institution

International Secretariat

PCT

(43) Date of being internationally (10) International Public

Public

Number

2001 12th July (12. 07. 2001) **WO 01 / 49640 A1**

<p>(51) International Patent Classification⁷: C 07 C 39/16, 37/20, C 07 B 61/00, B 01 J 31/08</p>	<p>PIN 130 - 0015, Tokyo to, Chuo ku, Kyobashi, 1 cho me, 6 ban, 1 go, Tokyo (JP).</p> <p>(72) Inventor ; as well as</p> <p>(75) Inventors / (Patent Applicants)</p>
<p>(21) International Patent Application</p>	<p>(Only with reference to the United States of America) [IWAHARA, Masahiro] [JP / JP]</p>

Number PCT/JP00/09405	PIN 754 - 0843, Yamaguchi ken, Tokuyama shi, Shinkyi machi, ban 1, go 1 Yamaguchi (JP).
(22) Date of International Patent Application 28 th December 2000 (28.12.00)	(74) Representative Patent Attorney (OHTANI, Tomotsu et. al) PIN 105 - 0001, Tokyo to, Minato ku, Seino kan 3 cho me, 8 ban, 27 go, Shinkoku machi, Annex Building number, 4 th floor, Tokyo (JP)
(25) Language of international application Japanese	(81) Indicated Countries (Domestic): BR, CN, ID, IN, JP, KR, SG, US.
(26) Language in which made internationally public Japanese	(84) Indicated Country (Wide Area): European Patents (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR)
(30) Preferential Claims Data Tokugan 2000 / 1824	

<p>1824</p> <p>7th January 2000</p> <p>(07.01.2000)</p> <p>JP</p> <p>(71) Patent Applicant</p> <p>(With reference</p> <p>to all the</p> <p>countries</p> <p>indicated in the</p> <p>list excluding the</p> <p>United States of</p> <p>America)</p> <p>(IDEMUTSU SEIYU</p> <p>KAGAKU KABUSHIKI</p> <p>KAISHA) (IDEMUTSU</p> <p>PETROCHEMICALS</p> <p>CO. LTD.) [JP</p> <p>/ JP]</p>	<p>Regarding 2 character code as</p> <p>well as abbreviation other</p> <p>than those, refer to the"</p> <p>Guidance Note of the code and</p> <p>abbreviations" that has been</p> <p>published in the beginning of</p> <p>the Gazette of the PCT that is</p> <p>regularly published.</p> <p>Additional Public Document:</p> <p>International Investigations</p> <p>(Search) Report</p>
<p>(54) Title : METHOD FOR MANUFACTURE OF BIS PHENOL A.</p>	

(57) Abstract

To offer a method for manufacture of bis phenol A, in which the life span of an acid type ion exchange resin that has been partially modified (denatured) by a sulfur containing amine compound that is used as catalyst, can be prolonged and by using which the bis phenol A can be obtained with a high productivity per catalytic unit. This method for manufacture of bis phenol A has the following characteristic. Namely, in this method in which the bis phenol A is manufactured by making the phenol and acetone to undergo a reaction using an acid type ion exchange resin that has been partially modified by the a sulfur containing amine compound, as catalyst and alkyl mercaptan as promoter (supporting catalyst), a multi-stage reaction vessel in which at least 2 units of reaction vessels have been arranged serially is used and moreover, the molar ratio of total alkyl mercaptan / total acetone as well as the molar ration of total acetone / phenol can be made to get increased by decreasing the conversion ratio of phenol.

A Detailed Description

Method for Manufacture of bis phenol A.

Technical Field

The present invention relates to the method for manufacture of bis phenol of A in which an acid type ion exchange resin that has been partially modified (denatured) by a sulfur containing amine compound that is used as catalyst, can be prolonged and by using which the bis phenol A can be obtained with a high productivity per catalytic unit. The bis phenol A is useful as a raw material in the method for manufacture of polycarbonate resin, epoxy resin, polyallylate resin etc.

Background techniques

The bis phenol A [2, 2 - bis (4 - hydroxy phenyl) propane] is known to be an important compound useful as a raw material in the engineering plastic such as polycarbonate resin or

polyallylate resin etc. or in the manufacture of epoxy resin etc. and in the recent years, the demand for the same has a tendency to increase still more.

This bis phenol A is known to be manufactured by making phenol and acetone to undergo a reaction using an acid type ion exchange resin that has been partially modified (denatured) by a sulfur containing amine compound and acidic cation exchange resin as catalysts and alkyl mercaptan as a promoter (supporting catalyst) (Refer to the patent bulletin of the Japanese public patent Hei 8 - 325185). However, the life span of the catalyst is short or the productivity of the bis phenol A per catalytic unit is less by adding only the alkyl mercaptan. Also, when the activity of catalyst is lowered, there do exist methods for the regeneration of this deteriorating catalyst by washing the same by using phenol or an acidic solvent. However, in this case, the productivity gets lowered and the treatment of the waste solvent of washing is difficult which is the problem

possessed by the same. Therefore, development of a method that can be used for manufacture of bis phenol A in which an acid type ion exchange resin that has been partially modified (denatured) by a sulfur containing amine compound that is used as catalyst, can be prolonged and by using which the bis phenol A can be obtained with a high productivity per catalytic unit is desired.

Display of the invention

The present invention has been devised by taking into consideration the points mentioned above and offer a method that can be used for manufacture of bis phenol A in which an acid type ion exchange resin that has been partially modified (denatured) by a sulfur containing amine compound that is used as catalyst, can be prolonged and by using which the bis phenol A can be obtained with a high productivity per catalytic unit.

The authors of the present invention carried out an

earnest research. As a result of the research carried out by them, they showed that the aim of the invention mentioned above can be effectively attained by using a multi-stage reaction vessel in which at least 2 units of reaction vessels have been arranged serially is used and moreover, the molar ratio of total alkyl mercaptan / total acetone as well as the molar ration of total acetone / phenol can be made to get increased by decreasing the conversion ratio of phenol. Along with showing the results mentioned above, the present invention was completed.

Namely, the gist of the present invention is as follows.

1. The method for manufacture of bis phenol A offered by the present invention has the following characteristic.
Namely, in this method in which the bis phenol A is manufactured by making the phenol and acetone to undergo a reaction using an acid type ion exchange resin that has been partially modified by the a sulfur containing amine compound, as catalyst and alkyl

mercaptan as promoter (supporting catalyst), a multi-stage reaction vessel in which at least 2 units of reaction vessels have been arranged serially is used and moreover, the molar ratio of total alkyl mercaptan / total acetone as well as the molar ratio of total acetone / phenol can be made to get increased by decreasing the conversion ratio of phenol.

2. The method for manufacture of bis phenol A offered by the present invention that has been described above in topic number 1, in which in the multi-stage reaction vessel that has been arranged in series, the entire quantity of phenol is supplied in 1 stage itself and the acetone is supplied in divided proportion (quantity) to each reaction vessel.
3. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 2, in which the molar ratio of total acetone / phenol in the initial stage of the

reaction is within the range from 1/9 to 1/11.

4. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 3, in which at the point of lowering the conversion ratio of the phenol occurring at the last emission port of the multi-stage reaction vessel to 90 to 99 % of that at the initial stage, the molar ratio of the total alkyl mercaptan / total acetone as well as molar ratio of the total acetone / phenol is made to get increased.
5. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 4, in which the molar ratio of total alkyl mercaptan / total acetone is made to get increased in such a range that it does not exceed 1/20.
6. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 5, in which the molar ratio

of total alkyl mercaptan / phenol is made to get increased in such a range that it does not exceed 1/3.

7. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 6, in which as regards the sulfur containing amine compound, mercaptoalkyl amine varieties or thiazolidine varieties are present.

8. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 7, in which as regards acid type ion exchange resin, sulfonic acid type cation exchange resin is present.

9. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the topics from 1 to 8, in which as regards the alkyl mercaptan, ethyl mercaptan is present.

10. The method for manufacture of bis phenol A offered by the present invention that has been described above in

any of the topics from 1 to 9, in which the temperature at which the reaction is carried out is within the range from 60 to 100°C.

Most desired state for the practicalization of the invention

A detailed explanation regarding the present invention has been presented below.

First, an explanation regarding the summary of the processing stages of the method for manufacture of bis phenol A has been presented.

Processing stage (1) (Processing stage of reaction)

The bis phenol A is manufactured by making acetone and excessive proportion of phenol to undergo a reaction by using acid type ion exchange resin as catalyst and alky mercaptan as promoter. As regards the acid type ion exchange resin that is being used as catalyst, generally sulfonic acid type cation exchange resins are desired to be used. As examples,

sulfonated styrene (styrene sulfonate) · di vinyl benzene copolymer, sulfonated bridging styrene copolymer (styrene sulfonate bridging copolymer), phenol formaldehyde sulfonic acid (phenol formaldehyde sulfonate) resin, benzene formaldehyde sulfonic acid (benzene formaldehyde sulfonate) resin etc. can be given. These can be used in a single type of the same or by combining more than 2 types.

As regards the examples for sulfur containing amine compound that modifies (denatures) the acid type ion exchange resin mentioned above, mercaptoalkyl amine varieties such as 2 - mercaptoethyl amine, 3 - mercaptoethyl amine etc., thiazolidine varieties such as 2, 2 - di methyl thiazolidine, 2 - methyl - 2 - ethyl thiazolidine, cyclo alkyl thiazolidine, 2 - methyl - 2 - phenyl thiazolidine, 3 - methyl thiazolidine etc., aminothiophenol varieties such as 1, 4 - aminothiophenol etc., mercaptoalkyl pyridine varieties such as 3 - mercaptomethyl pyridine, 3 - mercaptoethyl pyridine, 4 - mercaptoethyl pyridine etc. can

be given. However, among the examples described above also, mercaptoalkyl amine varieties and thiazolidine varieties are desired to be used. The proportion with which the sulfur containing amine compound mentioned above is used, is desired to be within the range from 2 to 50 mole % with respect to the sulfonic acid radical present within the acid type ion exchange resin, more desired it should be within the range from 5 to 30 mole % with respect to the sulfonic acid radical present within the acid type ion exchange resin.

The modification (denaturation) of the acid type ion exchange resin mentioned above can be carried out by making that resin and sulfur containing amine compound to undergo a reaction in water or an organic solvent. As regards the examples for organic solvent, phenol, acetone or methanol etc. can be used. However, it is desired to be carried out in water. As regards the temperature at which the reaction is carried out, either normal temperature (room temperature) or an elevated temperature is used. Moreover, the duration

of the reaction is not required to be particularly a longer duration and is sufficient to be of several tens of minutes. In order to make the reaction uniform, the reaction mixture is desired to be stirred.

As regards the alkyl mercaptan that is being used as a promoter, mercaptan having alkyl radical that has carbon atom from 1 to 10 is desired to be used. As examples, methyl mercaptan, ethyl mercaptan, propyl mercaptan, octyl mercaptan, cyclo hexyl mercaptan etc. can be given. However, ethyl mercaptan is particularly desired to be used. Moreover, these can be used in a single type of the same or by combining more than 2 types.

Other than bis phenol A, by-products such as unreacted phenol, unreacted acetone, water generated as a by-product, alkyl mercaptan as well as organic sulfur compound and colored materials etc. are contained within the reaction mixture.

Processing stage (2) (Processing stage of recovery of

water generated as a by-product and unreacted raw materials)

Next, the unreacted acetone, water generated as by-product as well as alkyl mercaptan etc. are removed from the reaction mixture obtained from the processing stage (1) by the process of distillation at reduced pressure from the top of the tower based on which liquid state reaction mixture containing bis phenol A as well as phenol etc. is obtained from the bottom of the tower. In the case of carrying out the process of distillation under reduced pressure, the conditions are practicalized with the pressure being within the range from 6.7 to 80.0 kPa and the temperature being within the range from 70 to 180°C. In this case, the unreacted phenol is subjected to the process of azeotropy and a part of it is removed out from the system from the top of the tower.

Processing stage (3) (Processing stage of concentrating the bis phenol A)

The phenol is removed by carrying out distillation under reduced pressure from the liquid present at the bottom of

the tower from which the materials of the types mentioned above have been removed from the reaction mixture and the bis phenol A is concentrated. This concentrated residual liquid becomes the raw material for the crystal deposition carried out in the next processing stage. There are no particular restrictions regarding the conditions under which the concentration is carried out. However, normally it is carried out under the conditions of the temperature being within the range from 100 to 170°C and pressure being within the range from 5.3 to 66.7 kPa. If the temperature at which the process of concentration is carried out becomes less than 100°C, then high degree of vacuum is required and if it becomes more than 170°C, then excessive heat is required to be removed in the next processing stage of crystal deposition. Also, the concentration of the bis phenol A present in the concentrated residual liquid should be within the range from 20 to 50 % by weight, desirably within the range from 20 to 40 % by weight. If this concentration becomes

less than 20 % by weight, then the ratio of recovery of bis phenol A becomes low and if it exceeds 50 % by weight, then the transfer of the slurry after the crystal deposition becomes difficult.

Processing stage (4) (Processing stage of crystal deposition)

The concentrated residual liquid obtained from the processing stage (3) is cooled upto the temperature within the range from 40 to 70°C. Then, the additive materials of bis phenol A and phenol (termed as phenol adduct from here onwards) are made to undergo crystal deposition and then, it becomes in the form of a slurry. The cooling is carried out by removing the heat by evaporation of water that has been added to the external part of heat exchange vessel or crystal deposition machine. Then, the concentrated residual liquid present in the form of a slurry is separated from the mother liquor of crystal deposition containing phenol adduct and by-products of the reaction by the process of filtration

or centrifugal separation etc. This mother liquor of crystal deposition is recycled immediately or in a partial manner into the reaction vessel and a part or entire part of it is made to undergo the process of alkali decomposition and is recovered as phenol and iso propenyl phenol. Also, a part or entire part of it can be recycled as raw material for the process of crystal deposition by isomerization (Refer to the patent bulletin of the Japanese public patent Hei 6 - 321834).

Processing stage (5) (Processing stage of fusion of phenol adduct by heating)

The crystals of adduct in which bis phenol A and phenol are present in 1 : 1 proportion that has been obtained from the processing stage (4) are fused by heating upto a temperature within the range from 100 to 160°C based on which it becomes into a form of a liquid state mixture.

Processing stage (6) (Processing stage of recovery of bis phenol A)

The phenol is removed from the liquid state mixture obtained from the processing stage (5) by the process of distillation under reduced pressure and the bis phenol A is recovered. The process of distillation under reduced pressure is carried out under the conditions of the pressure being within the range from 1.3 to 13.3 kPa and temperature being within the range from 150 to 190°C. Furthermore, the method for removal of phenol that is present in the form of a residual material carried out by steam stripping is also known.

Processing stage (7) (Processing stage of granulation of bis phenol A)

The bis phenol A present in the fused state material obtained from the processing stage (6) is subjected to the process of formation of liquid droplets by using granulation device such as spray drier etc. and it is solidified by cooling when it becomes a manufactured product. The liquid droplets are formed by spraying (atomization), dispersion

etc. and it is cooled by using nitrogen or air etc.

Next, a detailed explanation regarding the method of the present invention has been presented.

The present invention has the following characteristic. Namely, in the processing stage (1), a multi-stage reaction vessel in which at least 2 units of reaction vessels have been arranged serially is used and moreover, the molar ratio of total alkyl mercaptan / total acetone as well as the molar ratio of total acetone / phenol is made to get increased by decreasing the conversion ratio of phenol. The increased in the molar ratio of 2 mentioned above can be carried out in a continuous manner or in a stepwise manner.

As regards the reaction vessel, the multi-stage reaction vessel in which at least 2 units of reaction vessels have been arranged serially is used. The reaction of generation of bis phenol A is an exothermic reaction. Moreover, when the reaction vessel is made from 1 unit of reaction vessel, for removing the heat of the reaction, the structure of the

reaction vessel becomes complicated. Furthermore, when the heat is not removed, then the temperature of the same gets increased by the order of 10 to 20°C due to which temperature of usage of the ion exchange resin or the temperature that is appropriate to be used for the generation of the bis phenol A can easily exceeds by 55 to 95°C than their appropriate value due to which the inconvenience can get generated.

In the multi-stage reaction vessel mentioned above, the entire quantity of phenol is supplied in 1 stage itself and the acetone is supplied in divided proportion (quantity) to each reaction vessel as seen from the point of life span of the catalyst. Moreover, entire quantity of the alkyl mercaptan can be supplied in 1 stage itself or can be supplied in divided proportion (quantity).

Regarding the temperature at which the reaction is carried out, it is desired to be within the range from 60 to 100°C. If the temperature becomes exceedingly less, then the phenol phase solidifies. On the other hand, if becomes exceedingly

high, then there are cases of the deterioration of the ion exchange resin becoming high which is not desired. Furthermore, the desired temperature is within the range from 65 to 95°C.

The molar ratio of the total acetone / phenol in the initial stage of the reaction is desired to be within the range from 1/9 to 1/11. If it becomes more than 1/9, then there are cases the side reaction of acetone as well as phenol progressing upto a large extent whereas if it becomes less than 1/11, then the conversion ratio of the phenol standard becomes low and the proportion with which the phenol is recovered gets increased and moreover, there are cases of the productivity of bis phenol A getting lowered which is not desired.

In the present invention, it is required that, at the point of lowering the conversion ratio of the phenol occurring at the last emission port of the multi-stage reaction vessel to 90 to 99 % of that at the initial stage, the molar ratio

of the total alkyl mercaptan / total acetone as well as molar ratio of the total acetone / phenol is made to get increased. However, it is desired that, the molar ratio of the total alkyl mercaptan / total acetone is made to get increased in such a range that it does not exceed 1/20 and the molar ratio of the total acetone / phenol is made to get increased in such a range that it does not exceed 1/3. If it exceeds, then there are cases of the side reaction progressing upto a large extent which is not desired.

Moreover, the alkyl mercaptan can be added from the initial stage of the reaction or the addition can also be commenced at the stage at which the conversion ratio of phenol has begun to get lowered.

In the present invention, the reaction is carried out till the molar ratio of total alkyl mercaptan / total acetone becomes 1/20 or the molar ratio of the total acetone / phenol becomes 1/3 and then, the catalyst is exchanged.

Next, the present invention has been concretely explained

with the help of practical examples given below. However, it may be mentioned here that the present invention is not restricted only the cases of these practical examples.

[Practical example 1]

In a filling (packing) layer type reaction vessel having internal diameter of 13 mm. and height of 561 mm., sulfonic acid type cation exchange resin that was 20 % denatured (modified) by 2 - mercaptoethyl amine (74.4 mille liter swollen by phenol) (Mitsubishi Kagaku Shasei (Mitsubishi Chemicals Company make) dye (?) ion SK - 104H) was filled (packing). This reaction was serially connected with 2 units (of reaction vessels).

The liquid of phenol was made to flow at the rate of 4.68 mole / hour through the reaction vessel of stage number 1 and the liquid of acetone [molar ration of acetone / phenol = 1/20, molar ration of total acetone / phenol = 1/10] was made to flow at the rate of 0.234 mole / hour through the reaction vessel of stage number 1 as well as stage number

2 respectively and the reaction was carried out with the reaction temperature being maintained at 75°C. The reaction mixture was analyzed temporally and the conversion ratio of phenol was determined.

At the time of commencement of the reaction, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 6.0 % and (that of) reaction vessel of stage number 2 was 10.6 %.

① After the period of 600 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.8 % and (that of) the reaction vessel of stage number 2 was lowered to 9.7 % due to which the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 were replaced by the acetone containing ethyl mercaptan and moreover, the molar ratio of acetone / phenol was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/1,000

Molar ratio of acetone / phenol = 1.05/20

[Molar ratio of total acetone / phenol = 1.05 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 5.9 % and (that of) the reaction vessel of stage number 2 was 10.7 %.

② After the period of 1,300 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.6 % and (that of) the reaction vessel of stage number 2 was lowered to 9.3 % due to which the molar ratio of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/800

Molar ratio of acetone / phenol = 1.11/20

[Molar ratio of total acetone / phenol = 1.11 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number

1 was 6.1 % and (that of) the reaction vessel of stage number 2 was 10.6 %.

③ After the period of 2,000 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.3 % and (that of) the reaction vessel of stage number 2 was lowered to 9.1 % due to which the molar ratio of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/600

Molar ratio of acetone / phenol = 1.18/20

[Molar ratio of total acetone / phenol = 1.18 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 6.0 % and (that of) the reaction vessel of stage number 2 was 10.8 %.

④ After the period of 2,800 hours, (the conversion ratio

of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.2 % and (that of) the reaction vessel of stage number 2 was lowered to 9.3 % due to which the molar ratio of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/400

Molar ratio of acetone / phenol = 1.25/20

[Molar ratio of total acetone / phenol = 1.25 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 5.8 % and (that of) the reaction vessel of stage number 2 was 10.7 %.

⑤ After the period of 3,600 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.5 % and (that of) the reaction vessel of stage number 2 was lowered to 9.4 % due to which the molar ratio

of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/200

Molar ratio of acetone / phenol = 1.31/20

[Molar ratio of total acetone / phenol = 1.31 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 6.2 % and (that of) the reaction vessel of stage number 2 was 10.8 %.

⑥ After the period of 4,800 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.1 % and (that of) the reaction vessel of stage number 2 was lowered to 9.2 % due to which the molar ratio of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made

to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/100

Molar ratio of acetone / phenol = 1.39/20

[Molar ratio of total acetone / phenol = 1.39 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 6.0 % and (that of) the reaction vessel of stage number 2 was 10.6 %.

⑦ After the period of 5,700 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 3.9 % and (that of) the reaction vessel of stage number 2 was lowered to 9.0 % due to which the molar ratio of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/70

Molar ratio of acetone / phenol = 1.47/20

[Molar ratio of total acetone / phenol = 1.47 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 5.8 % and (that of) the reaction vessel of stage number 2 was 10.4 %.

⑧ After the period of 6,800 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 3.8 % and (that of) the reaction vessel of stage number 2 was lowered to 8.8 % due to which the molar ratio of ethyl mercaptan / acetone as well as molar ratio of acetone / phenol present in the reaction vessel of stage number 1 as well as the reaction vessel of stage number 2 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/40

Molar ratio of acetone / phenol = 1.55/20

[Molar ratio of total acetone / phenol = 1.55 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number

1 was 5.7 % and (that of) the reaction vessel of stage number 2 was 10.5 %.

The selectivity ratio of bis phenol A was within the range from 94.0 to 94.5 % till 6,800 hours from the commencement of the reaction.

[Practical example 2]

With reference to the processing carried out in the practical example 1 that has been described above, the 2 - mercaptoethyl amine was replaced by 2, 2 - di methyl thiazolidine and also, the reaction vessel was modified to 3 units arranged serially from 2 units arranged serially.

Furthermore, the liquid of acetone [molar ratio of acetone / phenol = 1/30, molar ratio of total acetone / phenol = 1/10] was made to flow at the rate of 0.156 mole / hour through the stage number 1, stage number 2 as well as stage number 3 respectively. Other than this change, all the constituents as well as the proportions of the constituents and conditions, which were used in the reaction, were kept the same and the

method identical one described above was practicalized. The reaction mixture was analyzed temporally and the conversion ratio of phenol was determined.

At the time of commencement of the reaction, (the conversion ration of phenol ? of) the reaction vessel of stage number 1 was 6.0 % and (that of) reaction vessel of stage number 2 was 10.4 % and (that of) reaction vessel of stage number 3 was 14.2 %.

① After the period of 900 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.3 % and (that of) the reaction vessel of stage number 2 was lowered to 9.4 % and (that of) the reaction vessel of stage number 3 was lowered to 13.9 % due to which the reaction vessel from stage number 1 to stage number 3 were replaced by the acetone containing ethyl mercaptan and moreover, the molar ratio of acetone / phenol of reaction vessel from stage number 1 to stage number 3 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/1,100

Molar ratio of acetone / phenol = 1.04/30

[Molar ratio of total acetone / phenol = 1.04 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 5.9 % and (that of) the reaction vessel of stage number 2 was 10.6 % and (that of) the reaction vessel of stage number 3 was 13.9 %.

② After the period of 1,900 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.1 % and (that of) the reaction vessel of stage number 2 was lowered to 9.1 % and (that of) the reaction vessel of stage number 3 was lowered to 13.5 % due to which the molar ratio of ethyl mercaptan / acetone of reaction vessel of stage number 1 as well as molar ratio of acetone / phenol of the reaction vessel from stage number 1 to stage number 3 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/800

Molar ratio of acetone / phenol = 1.15/30

[Molar ratio of total acetone / phenol = 1.15 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 5.8 % and (that of) the reaction vessel of stage number 2 was 10.4 % and (that of) the reaction vessel of stage number 3 was 14.2 %.

③ After the period of 3,000 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 4.0 % and (that of) the reaction vessel of stage number 2 was lowered to 9.0 % and (that of) the reaction vessel of stage number 3 was lowered to 13.3 % due to which the molar ratio of ethyl mercaptan / acetone of reaction vessel of stage number 1 as well as molar ratio of acetone / phenol of the reaction vessel from stage number 1 to stage number 3 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/400

Molar ratio of acetone / phenol = 1.26/30

[Molar ratio of total acetone / phenol = 1.26 / 10]

After the modification of the conditions, (the conversion ratio of phenol % of) the reaction vessel of stage number 1 was 5.7 % and (that of) the reaction vessel of stage number 2 was 10.2 % and (that of) the reaction vessel of stage number 3 was 14.1 %.

④ After the period of 4,200 hours, (the conversion ratio of phenol % of) the reaction vessel of stage number 1 was lowered to 3.8 % and (that of) the reaction vessel of stage number 2 was lowered to 8.7 % and (that of) the reaction vessel of stage number 3 was lowered to 12.9 % due to which the molar ratio of ethyl mercaptan / acetone of reaction vessel of stage number 1 as well as molar ratio of acetone / phenol of the reaction vessel from stage number 1 to stage number 3 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/200

Molar ratio of acetone / phenol = 1.57/30

[Molar ratio of total acetone / phenol = 1.57 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was 5.8 % and (that of) the reaction vessel of stage number 2 was 10.3 % and (that of) the reaction vessel of stage number 3 was 14.3 %.

⑤ After the period of 5,500 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 3.3 % and (that of) the reaction vessel of stage number 2 was lowered to 7.8 % and (that of) the reaction vessel of stage number 3 was lowered to 12.2 % due to which the molar ratio of ethyl mercaptan / acetone of reaction vessel of stage number 1 as well as molar ratio of acetone / phenol of the reaction vessel from stage number 1 to stage number 3 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/100

Molar ratio of acetone / phenol = 1.84/30

[Molar ratio of total acetone / phenol = 1.84 / 10]

After the modification of the conditions, (the conversion

ratio of phenol ? of) the reaction vessel of stage number 1 was 5.6 % and (that of) the reaction vessel of stage number 2 was 10.1 % and (that of) the reaction vessel of stage number 3 was 14.2 %.

⑥ After the period of 6,500 hours, (the conversion ratio of phenol ? of) the reaction vessel of stage number 1 was lowered to 2.9 % and (that of) the reaction vessel of stage number 2 was lowered to 7.1 % and (that of) the reaction vessel of stage number 3 was lowered to 11.9 % due to which the molar ratio of ethyl mercaptan / acetone of reaction vessel of stage number 1 as well as molar ratio of acetone / phenol of the reaction vessel from stage number 1 to stage number 3 was made to get increased as given below.

Molar ratio of ethyl mercaptan / acetone = 1/40

Molar ratio of acetone / phenol = 1.26/30

[Molar ratio of total acetone / phenol = 1.26 / 10]

After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel of stage number

1 was 5.3 % and (that of) the reaction vessel of stage number 2 was 9.7 % and (that of) the reaction vessel of stage number 3 was 14.1 %.

The selectivity ratio of bis phenol A was within the range from 94.0 to 94.5 % till 6,500 hours from the commencement of the reaction.

[Comparative example 1]

With reference to the reaction vessel used in the practical example 1, the reaction vessel having height of 561 mm. was replaced by the reaction vessel having height of 1.122 mm. and the reaction vessel in which 2 units (of reaction vessels) were arranged serially was replaced by 1 unit of reaction vessel.

Furthermore, the liquid of acetone [molar ratio of acetone / phenol = 1/10] was made to flow at the rate of 0.468 mole / hour through the reaction vessel. Other than this change, all the constituents as well as the proportions of the constituents and conditions, which were used in the reaction,

were kept the same and the method identical one described above was practicalized.

The reaction mixture was analyzed temporally and the conversion ratio of phenol was determined.

At the time of commencement of the reaction, (the conversion ration of phenol ? of) the reaction vessel was 10.6 %.

① After the period of 800 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 9.2 % due to which the reaction vessel was replaced by the acetone containing ethyl mercaptan [molar ratio of ethyl mercaptan / acetone = 1/500] . After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 10.5 %.

② After the period of 1,600 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 8.5 % due to which the concentration of ethyl mercaptan was made to get increased to 1/100 in terms of molar ratio of ethyl

mercaptan / acetone. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 10.2 %.

③ After the period of 2,200 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 7.8 % due to which the concentration of ethyl mercaptan was made to get increased to 1/50 in terms of molar ratio of ethyl mercaptan / acetone. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 10.0 %.

④ After the period of 2,900 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 7.1 % due to which the concentration of ethyl mercaptan was made to get increased to 1/20 in terms of molar ratio of ethyl mercaptan / acetone. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 9.7 %.

⑤ After the period of 3,400 hours, (the conversion ratio

of phenol ? of) the reaction vessel was lowered to 6.6 % due to which the concentration of ethyl mercaptan was made to get increased to 1/15 in terms of molar ratio of ethyl mercaptan / acetone. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 9.1 %.

⑥ After the period of 4,100 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 5.1 % due to which the concentration of ethyl mercaptan was made to get increased to 1/10 in terms of molar ratio of ethyl mercaptan / acetone. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 8.6 %.

⑦ After the period of 4,800 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 4.5 % due to which the concentration of ethyl mercaptan was made to get increased to 1/7 in terms of molar ratio of ethyl mercaptan / acetone. After the modification of the

conditions, (the conversion ratio of phenol ? of) the reaction vessel was 7.3 %.

[Comparative example 2]

With reference to the reaction vessel used in the practical example 1, the reaction vessel having height of 561 mm. was replaced by the reaction vessel having height of 1.122 mm. and the reaction vessel in which 2 units (of reaction vessels) were arranged serially was replaced by 1 unit of reaction vessel.

Furthermore, the liquid of acetone [molar ratio of acetone / phenol = 1/10] was made to flow at the rate of 0.468 mole / hour through the reaction vessel. Other than this change, all the constituents as well as the proportions of the constituents and conditions, which were used in the reaction, were kept the same and the method identical one described above was practicalized.

The reaction mixture was analyzed temporally and the conversion ratio of phenol was determined.

At the time of commencement of the reaction, (the conversion ratio of phenol ? of) the reaction vessel was 10.6 %.

① After the period of 800 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 9.2 % due to which the concentration of acetone was made to get increased to 1.21/10 in terms of molar ratio of acetone / phenol. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 10.5 %.

② After the period of 1,500 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 8.9 % due to which the concentration of acetone was made to get increased to 1.42/10 in terms of molar ratio of acetone / phenol. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 10.6 %.

③ After the period of 2,200 hours, (the conversion ratio

of phenol ? of) the reaction vessel was lowered to 8.1 % due to which the concentration of acetone was made to get increased to 1.63/10 in terms of molar ratio of acetone / phenol. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 10.2 %.

④ After the period of 3,000 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 7.7 % due to which the concentration of acetone was made to get increased to 1.92/10 in terms of molar ratio of acetone / phenol. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 9.9 %.

⑤ After the period of 3,500 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 7.0 % due to which the concentration of acetone was made to get increased to 2.22/10 in terms of molar ratio of acetone / phenol. After the modification of the conditions, (the

conversion ratio of phenol ? of) the reaction vessel was 9.3 %.

⑥ After the period of 4,000 hours, (the conversion ratio of phenol ? of) the reaction vessel was lowered to 6.7 % due to which the concentration of acetone was made to get increased to 2.56/10 in terms of molar ratio of acetone / phenol. After the modification of the conditions, (the conversion ratio of phenol ? of) the reaction vessel was 8.7 %.

As it can be understood from the practical example and comparative example, that by using the multi-stage reaction vessel in which at least 2 units of reaction vessels have been arranged serially and moreover, by making the molar ratio of total alkyl mercaptan / total acetone as well as the molar ration of total acetone / phenol to get increased by decreasing the conversion ratio of phenol, the life span of the catalyst can be conspicuously prolonged.

Industrial applicability

If the method of the present invention is used, then the life span of an acid type ion exchange resin that has been partially modified (denatured) by a sulfur containing amine compound that is used as catalyst, can be prolonged and by using which the bis phenol A can be obtained with a high productivity per catalytic unit.

Scope of patent claims

1. The method for manufacture of bis phenol A offered by the present invention has the following characteristic. Namely, in this method in which the bis phenol A is manufactured by making the phenol and acetone to undergo a reaction using an acid type ion exchange resin that has been partially modified by the a sulfur containing amine compound, as catalyst and alkyl mercaptan as promoter (supporting catalyst), a multi-stage reaction vessel in which at least 2 units

of reaction vessels have been arranged serially is used and moreover, the molar ratio of total alkyl mercaptan / total acetone as well as the molar ratio of total acetone / phenol can be made to get increased by decreasing the conversion ratio of phenol.

2. The method for manufacture of bis phenol A offered by the present invention that has been described above in claim number 1, in which in the multi-stage reaction vessel that has been arranged in series, the entire quantity of phenol is supplied in 1 stage itself and the acetone is supplied in divided proportion (quantity) to each reaction vessel.
3. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 2, in which the molar ratio of total acetone / phenol in the initial stage of the reaction is within the range from 1/9 to 1/11.
4. The method for manufacture of bis phenol A offered by

the present invention that has been described above in any of the claims from 1 to 3, in which at the point of lowering the conversion ratio of the phenol occurring at the last emission port of the multi-stage reaction vessel to 90 to 99 % of that at the initial stage, the molar ratio of the total alkyl mercaptan / total acetone as well as molar ratio of the total acetone / phenol is made to get increased.

5. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 4, in which the molar ratio of total alkyl mercaptan / total acetone is made to get increased in such a range that it does not exceed 1/20.
6. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 5, in which the molar ratio of total alkyl mercaptan / phenol is made to get increased in such a range that it does not exceed 1/3.

7. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 6, in which as regards the sulfur containing amine compound, mercaptoalkyl amine varieties or thiazolidine varieties are present.
8. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 7, in which as regards acid type ion exchange resin, sulfonic acid type cation exchange resin is present.
9. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 8, in which as regards the alkyl mercaptan, ethyl mercaptan is present.
10. The method for manufacture of bis phenol A offered by the present invention that has been described above in any of the claims from 1 to 9, in which the temperature at which the reaction is carried out is within the range

from 60 to 100°C.